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Using visible and ultraviolet light to drive the reduction of nitroaromatics to azo compounds on supported gold nanoparticles

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Photocatalytic processes have attracted significant interest since 1970's and are still very active research areas today [1,2]. The degradation of organic pollutants and the production of hydrogen and oxygen from water with semiconductor photocatalysts such as TiO_2, ZnO and CdS have been extensively studied. However, there are few studies on the photocatalytic reactions of organic synthesis under visible light with new catalysts such as gold nanoparticles (AuNPs). While fine gold particles have adorned some of the most majestic stained glass windows of medieval churches for centuries, researchers have only recently discovered two of their most significant properties [3]. Firstly, at elevated temperatures they can catalyse many reactions of organic compounds including the oxidation of various organic compounds and the reduction of nitrobenzene [4-6]. Secondly, AuNPs can strongly absorb visible light due to the surface plasmon resonance (SPR) effect [7-11]. The SPR effect is the collective oscillation of conduction electrons in the nanoparticles (NPs), which resonate with the electromagnetic field of the incident light. This gives rise to a significant enhancement of the local electromagnetic fields near the rough surfaces of the AuNPs. As a result of the SPR effect, light absorption for typical spherical AuNPs is generally observed between 520 and 550 nm [5], which can generate energetic electrons in the AuNPs and cause rapid heating of the NPs [12]. Together, these two properties offer an interesting hypothesis: the molecules on the AuNPs can be activated for reaction by the light-heated AuNPs and their interaction with energetic electrons in the AuNPs. This means that we may be able to drive reactions on the AuNPs using visible light at ambient temperature. The AuNPs also exhibit significant ultraviolet (UV) absorption that causes an interband excitation of electrons from 5*d* to 6*sp* [10,13,14]; this may also be used to drive chemical reactions. Given that visible light (wavelength 400-700 nm) and UV irradiation (wavelength < 400 nm) constitute around 43 % and 4% of the solar energy emitted by the sun, respectively [15], a photocatalytic process with supported AuNP photocatalysts has the potential to use sunlight — an abundant and green energy source — to drive chemical reactions efficiently. Light absorption by AuNPs is also a local effect limited to gold particles such that light only heats the AuNPs, which generally account for a few percent of the overall catalyst mass [4-6,16,17]. Therefore, such a process, if successfully realised, can be conducted at ambient temperature. This implies that this photocatalytic process can produce compounds that would have been unstable intermediates in a thermal reaction at high temperature.

Aromatic azo compounds are widely used for producing dyes, food additives and pharmaceutical products [5,18]. Currently, the synthesis of these compounds is often conducted under high pressure and temperature using transition metal reducing agents. The by-products formed from the reducing agent are of environmental concerns. Recently, it was reported that aromatic azo compounds could be synthesized from the corresponding nitroaromatic compounds through a two-step, one-pot reaction with catalysts of AuNPs on TiO_2 or CeO_2 at 100 °C or above [6]. First, nitrobenzene was over-reduced to aniline by hydrogen at a pressure of 9 bar on the gold catalysts. Then the reaction was brought back by flushing out the H_2 and introducing O_2 at 5 bar to oxidize aniline to yield azobenzene at 100 °C. Azobenzene was formed in the thermal hydrogenation of nitrobenzene as an intermediate to aniline, but was unstable under the reaction conditions and so rapidly reduced to aniline [6,17]. A subsequent oxidation step was required to bring to the product azobenzene. As photocatalytic reactions are mostly conducted at ambient temperature and atmospheric pressure [1,2], many intermediates are stable under such conditions and would not react further. If the direct reduction of nitroaromatic compounds to their corresponding azo aromatic compounds can be realised by a photocatalytic process, the synthesis of aromatic azo compounds would be a much more controlled, simplified and greener process.

To test the possibility of driving nitrobenzene reduction with light, AuNPs were supported on zirconia powder by reducing $HAuCl_4$ with $NaBH_4$ in the presence of ZrO_2 powder (full details of the synthesis and characterization are given in the Method Summary). Photocatalysts with three gold loadings (1.5, 3.0 and 5.0 % of the overall catalyst mass, expressed in wt%) on the ZrO_2 powder were prepared. Transmission electron microscopy (TEM) images of these samples showed that gold existed as nanoparticles of about 6 nm in size on ZrO_2 (Figure 1). These catalysts were used directly for photocatalytic reactions. Table 1 summarizes the catalysts' performances in reducing nitroaromatic compounds in an isopropanol solution under the illumination of incandescent light – mainly composed of visible light (see Figure S1, Supplementary Information, SI) – in argon atmosphere.

The photocatalytic reduction of nitrobenzene achieved a high conversion of nitrobenzene and a high selectivity to the target product, azobenzene, when illuminated with light of wavelengths > 400 nm and intensity of 0.30 W/cm^2 (measured at the reaction system). In 5 hours, 100 % of nitrobenzene was reduced and more than 99 % of the product was azobenzene. The highest activity was exhibited by the photocatalyst with a gold content of 3 wt%. Photocatalysts with a lower or higher gold content (1.5 wt% or 5 wt%) exhibited clearly a poorer performance (see Table in SI). A gold loading higher than 3 wt% leads to an aggregation of the NPs, according to the TEM observation (not present). This reduces the surface of the AuNPs, on which the catalytic reaction takes place. The temperature of the reaction system was 40 °C, slightly above ambient temperature, due to irradiation. A control experiment

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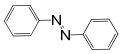
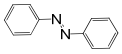
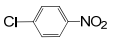
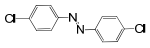
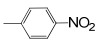
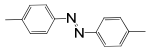
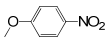
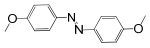
showed that a negligible reduction of nitrobenzene occurred in the dark at 40 °C. No reaction was observed in a blank experiment conducted in the absence of the AuNPs under otherwise identical conditions with ZrO_2 powder. Furthermore, when light intensity was reduced from 0.30 W/cm^2 to 0.15 W/cm^2, 0.03 W/cm^2 and 0.017 W/cm^2 with other experimental conditions unchanged, the conversion activity of nitrobenzene decreased from 100% to 76.5%, 50% and 30%, respectively. Evidently, the reduction was driven by visible light.

The new photocatalyst also promoted the reduction of other nitroaromatic compounds exhibiting high conversion activity and high selectivity to the corresponding azo compounds (Table 1).

Table 1. Reduction of nitroaromatic compounds in the presence of supported metal nanoparticles as catalyst.[a]

Reactant	Main product	Conv. %	Sel. %	Photonic efficiency %
		100[b1]	>99	6.9
		100[b2]	95	7.3
		100[b3]	56	3.6
		58[b3]	>99	2.1
		100[b3]	82	3.6

[a] Reduction reaction was conducted in an argon atmosphere at 40 °C using 30 mL of isopropanol as the solvent mixed with 0.3 mmol KOH solution, 3 mmol nitrobenzene, and 100 mg catalyst. [b1] Reaction time, 5h. [b2] Reaction time, 3h. [b3] Reaction time, 6h.

The photonic efficiency of the reduction could be estimated from the radiation absorbed by the photocatalyst [19]. Details of the measurement and calculation of the photonic efficiency of the current study are given in Figure S1. The efficiency was 6.9% for nitrobenzene reduction using 3 wt% AuNPs supported on ZrO_2, exceeding that of the well-known photocatalysis which uses TiO_2 catalyst under UV irradiation (efficiency <1.5%). The AuNP photocatalysts are able to catalyse the reduction of 0.1 mol/L nitrobenzene (the molar ratio of reacted nitrobenzene to gold in the photocatalyst is 197).

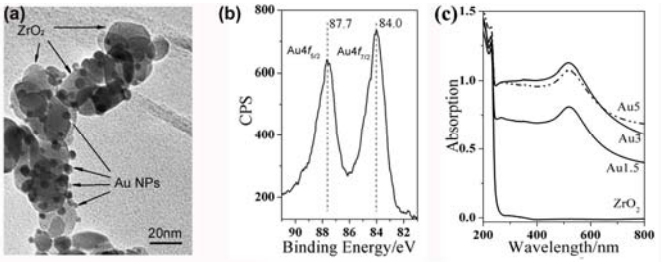


Figure 1. Catalyst characterization. (a) TEM image of 3 wt% Au/ZrO_2 (3 wt% of gold nanoparticles on ZrO_2); (b) X-ray photoelectronic spectra (XPS) of 3 wt% Au/ZrO_2 and (c) UV-Visible diffuse reflectance spectra of the ZrO_2 support and 3 wt% Au/ZrO_2 photocatalysts.

The XPS spectra of the supported gold photocatalysts with different gold contents all exhibited the same pattern. The binding energies of Au $4f_{7/2}$ and Au $4f_{5/2}$ electrons are 84.0 eV and 87.7 eV (Figure 1b), respectively. These are identical to the gold metal and suggest that gold exists in the metallic state in the photocatalysts. Therefore, the absorption peak at ~520 nm in the UV-Visible spectrum of the gold supported on ZrO_2 (Figure 1c) can be attributed to a SPR absorption by the AuNPs; since ZrO_2 exhibited little absorption of light with wavelengths longer than 330 nm. The band gap of ZrO_2 is about 5 eV [20]. These results further confirm the conclusion that the AuNPs supported on ZrO_2 were the photocatalysts and the reduction of nitroaromatic compounds was driven by visible light. More details on the consideration of the choice of oxide support are provided in Supplementary Information.

The significant UV absorption of AuNPs (Figure 1c) can drive the photocatalytic reduction of nitrobenzene, too. The conversion of nitrobenzene under UV irradiation with an intensity of 0.017 W/cm^2 was found to be 36%, which is higher than that under visible light of the same intensity (30%). This demonstrates that the wavelength of the irradiation can influence the reaction rate of the photocatalytic reduction.

Gaseous oxygen was released as an unforeseen by-product. A pre-vacuumed gas expansion bag was connected with the sealed round-bottom flask to collect the released gas throughout the photocatalytic reduction. The specimens of the gas in the bag were analysed using gas chromatography (GC, Shimadzu GC-2014 with 5A molecular sieve column). The quantity of the released O_2 gas was estimated from its volume, being equivalent to about 82 ± 5% of the amount derived from the quantity of the reacted nitrobenzene. Release of O_2 gas has not been observed in such reduction under thermal reaction conditions. Evidently, the photocatalytic reduction proceeded in a mechanism different from that of conventional reduction or catalytic reduction in a thermal reaction process.

We also found that the solvent affected reduction activity substantially. Solvents such as ethanol, iso-butanol, benzyl alcohol and hexyalcohol were used but the best performance was achieved with isopropanol. For example, the reduction in isobutanol attained only 30% of conversion and 60% of selectivity on the 3 wt% Au/ZrO_2 photocatalyst after 5 hours with other experimental conditions unchanged. It has been documented that isopropanol can be oxidized to acetone in a catalytic reaction with heating, thereby effecting the simultaneous reduction of the compound dissolved in it [21]. If isopropanol was involved in this study as a reducing agent, the reaction would be:

$$2\ \text{Ph-NO}_2 + 4\,\text{H}_3\text{C}-\underset{\text{H}}{\overset{\text{OH}}{\text{C}}}-\text{CH}_3 \longrightarrow \text{Ph}-\text{N}=\text{N}-\text{Ph} + 4\,\text{H}_3\text{C}-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{CH}_3 + 4\text{H}_2\text{O} \qquad (1)$$

Careful analysis of the product using an Agilent HP-6890 gas chromatography with DB-Wax column confirmed the formation of acetone during the reaction. However, the amount of acetone was only 1/8 of the quantity calculated from Eq.(1). It was also noted that most of the acetone in the reaction system was formed in the first hour of the reaction. Thereafter, the amount of acetone remained almost constant even though the reaction proceeded further to produce more of the product, azobenzene (Figure 2).

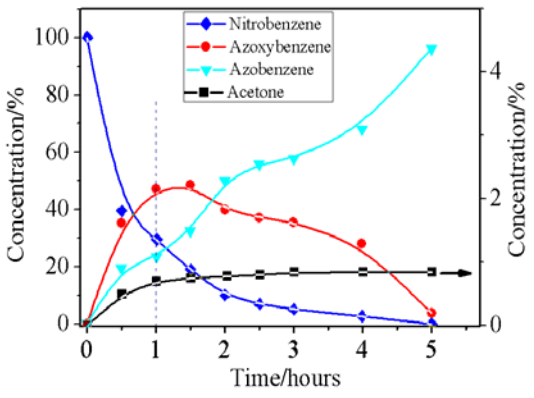
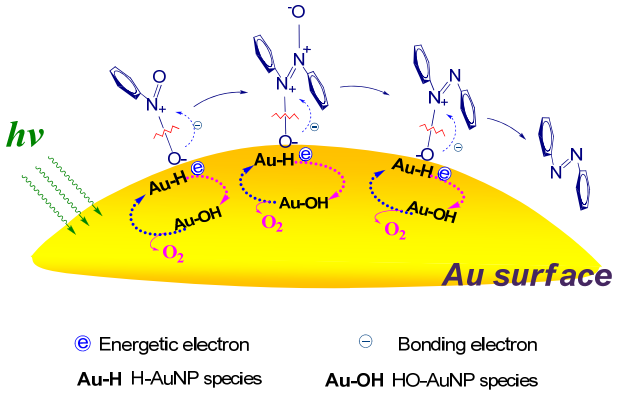


Figure 2. Time-conversion plot for nitrobenzene reduction and acetone formation with a catalyst of 3 wt% Au/ZrO_2 and irradiation intensity of 0.3 W/cm^2. Reduction reaction was conducted in an argon atmosphere at 40 °C using 30 mL isopropanol as the solvent mixed with 0.3 mmol KOH solution, 3 mmol substrate, and 100 mg catalyst. The axis on the right hand side refers to the content of acetone, which is below 1%.

Hence, isopropanol appeared as an initiator only, which initiated the reaction but did not involve in the reactions afterward. Clearly, the photocatalytic reaction, especially after the first hour, did not proceed according to Eq.(1). This reaction should involve two processes. In the first process (the reaction in the first hour), isopropanol was oxidized. In the second process (the reaction after the first hour), the production of aromatic azo compounds proceeded with species formed in the first process but did not rely on the oxidation of isopropanol.

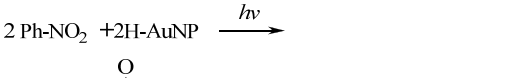
Isopropanol is a hydrogen-donor solvent, and the presence of KOH enhances the abstraction of hydrogen from isopropanol [22]. Indeed, species of hydrogen atom bonded to AuNP surface (H-AuNP) have been detected from supported AuNPs in the presence of isopropanol [23]. The Au-H bond is relatively stable. Hence, H-AuNP species can form on the surface of AuNPs in the reaction system of the present study. These species are capable of combining with the oxygen atoms of N-O bonds to yield HO-AuNP species. The energetic electrons excited by the light absorption of AuNPs can provide the activation energy that is required for the cleavage of the N-O bond. The existence of HO-AuNP species has been reported by other researchers [24]. The HO-AuNP species can release oxygen gas and transform to H-AuNP species that are recycled in the subsequent reaction process (see Scheme 1)



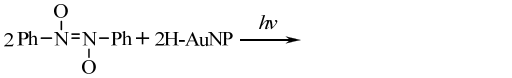
Scheme 1. The mechanism for the photocatalytic reduction of nitroaromatic compounds. H-AuNP reacts with the N-O bonds, yielding HO-AuNP species. HO-AuNP species subsequently decompose to yield oxygen molecules and H-AuNP species.

With the species found in the present study and reported in the literature, we tentatively propose the elementary reactions that may be involved in this photocatalytic process:

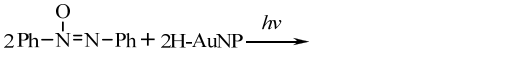
(2)



(3)

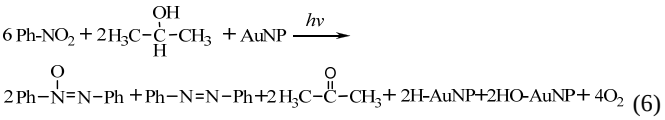


(4)



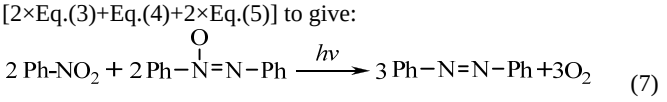
(5)

As shown in Figure 2, the ratio between the contents of azoxybenzene and azobenzene was approximately 2:1 after the first hour of reaction. Thus, the overall reaction of the first process can be derived by summing the above elementary reactions [2×Eq.(2)+4×Eq.(3)+3×Eq.(4)+Eq.(5)] to give:



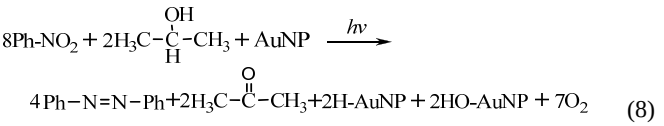
(6)

In the second process, the oxidation of isopropanol was negligible and a large amount of azoxybenzene formed in the first process (Figure 2) was reduced. Hence, we exclude reaction of Eq.(2) and sum up the elementary reactions [2×Eq.(3)+Eq.(4)+2×Eq.(5)] to give:



(7)

The above equation suggests that an intra-molecular oxidation/reduction of nitrobenzene and azoxybenzene took place in the second stage. Oxygen atoms in the nitro compound molecules, which were in an oxidation state of -2, were oxidized to oxygen molecules (a state of 0). Meanwhile the nitrogen atoms were reduced from an oxidation state of +3 to a state of -1. Summing up reactions of Eqs.(6) and (7), the reaction for the overall photocatalytic process is:



(8)

The molar ratio of azobenzene to acetone (2:1) and the amount of oxygen released (87.5% of the mole number of the reacted nitrobenzene) in this equation are consistent with the experimental results (82 ± 5%). Azoxybenzene, produced by the removal of a single oxygen atom from the dimeric structure of nitrosobenzene, was detected in this study. Figure 2 shows its content during the reaction. Azoxybenzene lost the oxygen atom of the N-O bond in the subsequent step [Eq.(5)], yielding the final product, azobenzene. The product of reactions [Eqs.(2) and (3)], the dimeric structure of nitrosobenzene, was also reported in the literature [25].

According to Eq.(2), the oxidation of isopropanol yields H-AuNP species. After the initial reaction stage, the oxidation of isopropanol should cease when the surface of AuNPs in the reaction system becomes saturated with H-AuNP and HO-AuNP species, and the content of acetone remains unchanged. It follows that the amount of acetone, the product of the first reaction process, should be in direct proportion to the quantity of AuNPs in the reaction system. Indeed, when the quantity of the photocatalyst, which is proportional to the surface area of AuNPs, increased from 100 mg to 200 mg, the content of acetone in the reaction system doubled after one hour of reaction.

According to Scheme 1, the H-AuNP species play a pivotal role in this photocatalytic reaction. It is, therefore, expected that the removal of the species would prohibit the reaction. 2,2',6,6'-tetramethylpiperidine N-oxyl (TEMPO) is a hydrogen abstractor and can abstract hydrogen atoms from the surface of gold to form hydroxylamine [26]. When 200 mg of TEMPO was added to the reaction system with 100 mg of 3 wt% Au/ZrO_2 photocatalyst there was almost no nitrobenzene reduction. We did not detect any products or intermediates of the reactions between TEMPO and reactant. This result confirms the existence and role of H-AuNP species in the systems of the present study. To further verify the important role of the H-AuNP and HO-AuNP species, 3 mmols of fresh nitrobenzene was injected into a sealed reaction system in which an initial reactant of 3 mmol nitrobenzene had been converted to the product, azobenzene, after 5 hours of reaction. Two hours

later, more azobenzene and azoxybenzene formed with a negligible increase of acetone. Evidently, the conversion of the injected nitrobenzene was mainly due to the H-AuNP and HO-AuNP species.

The role of the H-AuNP and HO-AuNP surface species provides explanation for the lower activity of the sample with larger AuNPs (obtained by heating the 3 wt% AuNPs on ZrO_2). With reduced surface area, the number of surface species also reduced resulting in poorer performance. It is also known that AuNPs smaller than 2 nm exhibit very weak SPR effect [27]. The mean size of the AuNPs (3 wt%) on ZrO_2 was ~ 6 nm so that they have a large surface to accommodate the surface species and good SPR light absorption. Hence the photocatalyst exhibited relatively high activity.

The key step of the reduction is to break the N-O bonds. The electrophilic N-O bond cleavage was realized by the H-AuNP species, and preferred an environment with energetic electrons as provided by the illuminated AuNPs. The absorption of visible light by AuNPs through the SPR effect caused changes in the electron distribution over the energy levels. The 6*sp* electrons of gold gained energy through SPR absorption and migrated to higher energy levels [9,11,13,14] (left panel, Scheme in SI). UV irradiation can also generate energetic electrons via an interband excitation of electrons from 5*d* to 6*sp* (right panel, Scheme in SI).

These energetic electrons interact strongly with the electrophilic nitro-groups of the nitrobenzene molecules, assisting the cleavage of the N-O bonds by H-AuNP species on the AuNPs (Scheme 1). Increasing the irradiation intensity produces more energetic electrons. To verify the important role of the energetic electrons further, in one experiment light irradiation was turned off after the reaction proceeded for 1.5 hours. In such a reaction system, there were sufficient H-AuNP species but no energetic electrons. The reaction did not proceed further. Without the energetic electrons (under dark condition), these species could not break the N-O bonds.

The most outstanding feature of the new photocatalysts is their moderate ability in catalysing redox reactions. The well-known TiO_2 semiconductor photocatalysts has a high oxidative potential (2.7 V) [4]. They generally exhibit poor selectivity, making them a poor choice for catalytic synthesis of fine chemicals. It is also difficult to adjust the oxidative potential of the semiconductor photocatalysts in order to tune its selectivity. In contrast, the moderate catalysing power of the supported AuNPs photocatalysts combined with the ability to conduct photocatalytic reduction at lower temperature and pressure than those for thermal reactions, they have enabled us to select an unstable intermediate of a thermal reaction as the product, such as the aromatic azo compounds. This discovery reveals a new class of useful catalytic processes for fine chemical production. These are greener processes with the potential to utilise solar energy and be applied in temperature-sensitive synthesis.

Experimental Section

Catalyst preparation: 2.5 g of ZrO_2 powder (particle size less than 100 nm) was dispersed into 93 mL of a given concentration of $HAuCl_4$ solution. 20 mL of 0.53 M lysine was then added into the mixture with vigorous stirring for 30 min. To this suspension, 10 mL of 0.35 M $NaBH_4$ solution was added gradually, followed by an addition of 10 mL of 0.3 M hydrochloric acid. The mixture was aged for 24 h and then the solid was separated, washed with water and ethanol, and dried at 60 °C. The dried solid was used directly as catalyst.
Activity test: Reduction of nitrobenzene was conducted in an argon atmosphere at 40°C unless otherwise specified. 3 mmol nitrobenzene was dissolved into 30 mL of isopropanol, into which 3 mL of 0.1 M KOH solution in isopropanol and 100 mg of the catalyst were added. The mixture was stirred with a magnetic stirrer during reaction and illuminated with incandescent light or UV light. The gaseous samples were analyzed by Shimadzu GC-2014 with 5A molecular sieve column and the liquid products were analyzed by a GC (Agilent HP-6890) with DB-Wax column.
Characterisation: TEM images were taken with a Philips CM200 Transmission electron microscope employing an accelerating voltage of 200 kV. The specimens were fine powders deposited onto a copper microgrid coated with a holey carbon film. The composition of some samples was determined by energy-dispersive X-ray spectroscopy attached on an FEI Quanta 200 scanning electron microscope. The diffuse reflectance UV-Visible spectra of the samples were recorded on a Cary 5000 UV-Vis-Nir Spectrophotometer.

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Entry for the Table of Contents (Please choose one layout)

Layout 2:

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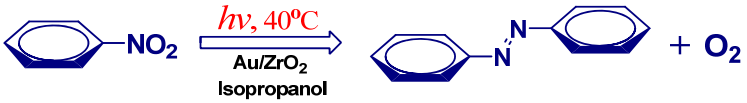


Using visible and ultraviolet light to drive the reduction of nitroaromatics to azo compounds on supported gold nanoparticles

((Text for Table of Contents, max. 450 characters)) Nitroaromatics in isopropanol solution can be reduced directly to the corresponding azo compounds on gold nanoparticles (3 wt%) supported on ZrO_2 with high selectivity when illuminated with visible light or ultraviolet light at 40°C. This discovery reveals the potential for utilising sunlight to drive the production of fine chemicals and enable us to select the unstable intermediate in the thermal reactions as the product. This green process can be applied to temperature-sensitive synthesis.

Supplementary Information

Using Visible and Ultraviolet Light to Drive the Reduction of Nitroaromatics to Azo Compounds on Supported Gold Nanoparticles

This file includes:

- The measurement and calculation of the photonic efficiency in the current study
- Figure S1
- The choice of the oxide support
- The influence of the gold contents on activity and selectivity of nitrobenzene reduction
- Electron excitation in AuNPs due to light absorption.

The measurement and calculation of the photonic efficiency in the current study

The light intensity measured at the reaction system was 0.30 W/cm^2, which included both the absorbed and scattered light. The overall energy of the photons of the irradiation on the reaction system was derived from the product of the light intensity and the cross-section area of the reactor, which was under irradiation. The overlap of the light source and the absorption spectrum of catalysts provide the distribution of the absorbed photons over the wavelength range between 400 nm and 800 nm (Figure S1). We estimated the mean wavelength of the absorbed photons from the distribution (after being normalized). The mean energy of the photons was calculated from the mean wavelength. The number of photons introduced into the reaction system was calculated from the ratio of the overall energy of the photons and the mean energy of the photons. The number of molecules formed was determined during the course of the reaction. Thus, the photonic efficiency was derived from the ratio of the number of molecules formed to the number of the photons introduced into the reaction system.

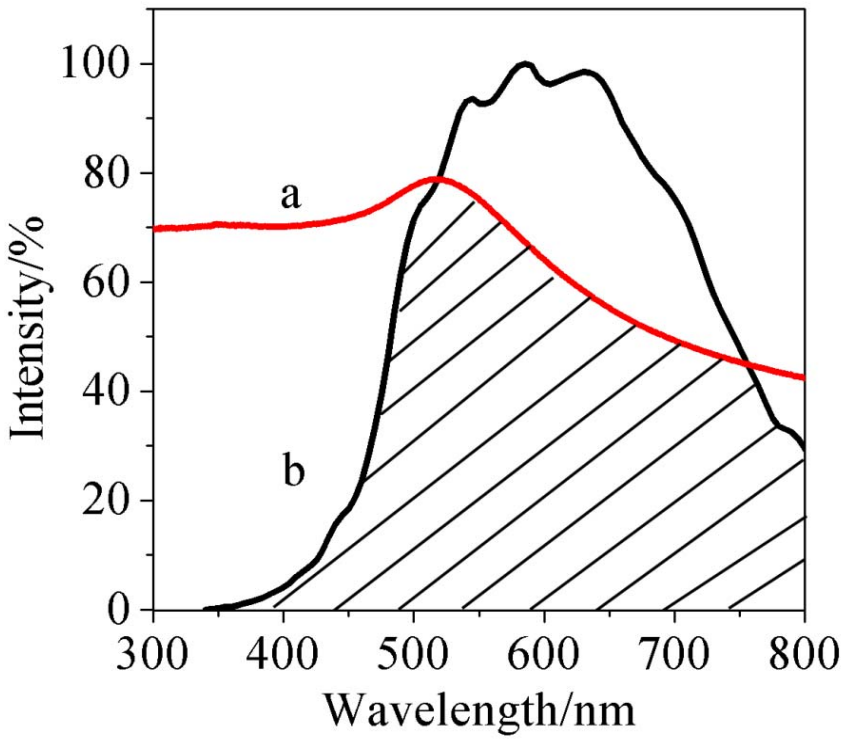


Figure S1. Absorption intensity of gold nanoparticles on ZrO_2 (a), and irradiation intensity of incandescent light (b).

The photonic efficiency in this study was relatively high. For example, using a 3 wt% Au/ZrO_2 photocatalyst the photonic efficiency was 6.9% for the nitrobenzene reduction, which exceeded the yield for a common photocatalysis using TiO_2 catalyst under UV irradiation (photonic efficiency < 1.5%). The high efficiency was consistent with the experience that TiO_2 photocatalysts were generally used to degrade trace amounts of pollutants and that the AuNP photocatalysts were able to catalyse the reduction of 0.1 mol/L nitrobenzene.

The influence of the gold contents on activity and selectivity of nitrobenzene reduction

Table. The activity and selectivity of the AuNPs catalysts with various gold contents for nitrobenzene reduction.[a]

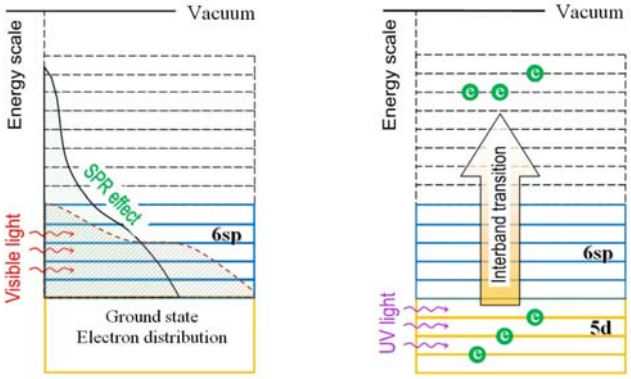
Catalysts	Conversion %[b]	TON[c]	Selectivity %
1.5 wt%Au/ZrO_2	59	233	88
3 wt% Au/ZrO_2	100	139	>99
5 wt% Au/ZrO_2	69	81	82

[a] Reaction was conducted in an argon atmosphere at 40°C using 30 mL of isopropanol as the solvent mixed with 0.3 mmol KOH solution, 3 mmol nitrobenzene, and 100 mg catalyst.[b] Reaction time, 5h. [c] Turnover number (TON) was calculated using the catalysts' gold content and nitrobenzene conversion. It indicates the number of nitrobenzene molecules converted on one gold atom during the reaction (5 hours).

The choice of the oxide support

The current study did not emphasise the role of the support due to space limitation and its comparatively lesser importance than other factors in the reaction process. The main consideration on the choice of the support was whether gold nanoparticles could be distributed over the support surface homogeneously and bond to the surface solidly. For instance, gold nanoparticles formed on silica particulates are not uniform and drop off easily during long periods of stirring. This would cause serious changes if photocatalysts of gold on silica were reused. Also, porous solids were not used because the porosity may have additional influences.

Electron excitation in AuNPs due to light absorption.



Scheme. Electron excitation in AuNPs due to the SPR effect when illuminated with visible light (left), and due to an interband transition when illuminated with UV light (right). The 6sp electron occupancy obeys the Fermi-Dirac distribution [13] but the SPR absorption of AuNPs changes the distribution. UV light absorption by AuNPs (shown in Figure 1c) can excite 5d electrons to high 6sp energy levels. The absorption of both lights results in energetic electrons on the AuNP surface. The relaxation of the energetic electrons from high to low energy levels is fast [17], however, the constant irradiation of light during the reaction should maintain the 6sp electron occupancy at high energy levels (a small number of electrons).